



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 413 029 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: 90901007.6

(51) Int. Cl.⁵: C22C 1/02, H01M 4/38

(22) Date of filing: 28.12.89

(96) International application number:
PCT/JP89/01319

(97) International publication number:
WO 90/07585 (12.07.90 90/16)

(30) Priority: 29.12.88 JP 333227/88
29.12.88 JP 333228/88

(43) Date of publication of application:
20.02.91 Bulletin 91/08

(94) Designated Contracting States:
DE FR GB

(71) Applicant: MATSUSHITA ELECTRIC
INDUSTRIAL CO., LTD
1006, Ohaza Kadoma, Kadoma-shi
Osaka 571(JP)

(72) Inventor: GAMOU, Takaharu
12-3, Kasugaoka 3-chome Fujiidera-shi
Osaka 583(JP)
Inventor: MORIWAKI, Yoshio

13-14, Minamifunahashi 2-chome
Hirakata-shi
Osaka 573(JP)
Inventor: IWAKI, Tsutomu
26-193, Hashimoto-Kurigatani Yawata-shi
Kyoto 614(JP)
Inventor: SHINTANI, Akemi 13-6,
Minamitchioka 2-chome
Minato-ku Osaka-shi
Osaka 552(JP)

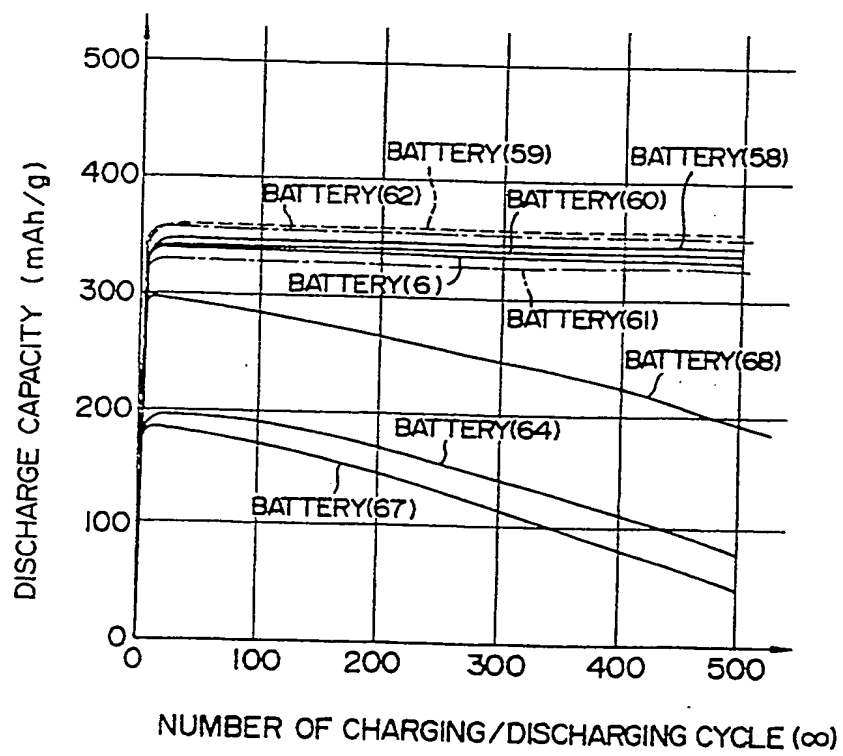
(74) Representative: Graf von Wengersky, Anton et
al
Patentanwälte Leinweber & Zimmermann
Rosental 7
D-8000 München 2(DE)

(54) METHOD OF PRODUCING HYDROGEN-OCCLUSION ALLOY AND ELECTRODE USING THE ALLOY.

(57) According to this invention, part or the whole of elementary Zr as a starting material for producing alloy is substituted by ferrozirconium (Zr-Fe alloy) or zircalloy (Zr-Sn alloy) in order to obtain a hydrogen-occlusion alloy at a reduced raw material cost and a reduced manufacturing cost, maintaining good operation efficiency, high reliability and safety in operation. The alloy is homogeneous without segregation and, hence, is featured by very good properties specific to the hydrogen-occlusion alloy such as amount of hydrogen occlusion, reaction rate and electrode reaction efficiency in the electrolyte. Using the alloy obtained by this method, furthermore, it is possible to provide a nickel-hydrogen storage cell which has a large electric capacity, can be quickly charged and discharged, has a long life and is advantageous in economy.

EP 0 413 029 A1

FIG. 1



METHOD OF PRODUCING HYDROGEN-STORING ALLOY AND ELECTRODE MAKING USE OF THE ALLOY

Technical Field

The present invention relates to a method of producing a hydrogen-storing alloy which is capable of reversibly storing and releasing large quantity of hydrogen, and also to a storage battery electrode making use of the alloy.

Background Art

Hitherto, hydrogen-storing alloys of the kinds containing rare earth elements or Zr(Ti) or Mg have been known as materials used for storage, holding and transportation of hydrogen, heat pumps, alkali storage batteries, and so forth. Among these alloys, alloys of Zr(Ti)-Ni, Zr(Ti)-Fe, Zr(Ti)-V and Zr(Ti)-Sn, as well as alloys containing many elements which are based on these alloys with part of elements replaced with other element or with addition of another element, are attracting attention because these alloys are superior in hydrogen storage capacity, reaction speed, hydrogen-dissociating equilibrium pressure, safety in terms of flammability in air, and electrochemical hydrogen storage and release characteristics. More specifically, Zr-containing Laves-phase alloys (AB₂ type alloy: A and B representing different elements) are suitable for practical use because they can safely store and release large quantity of hydrogen.

In general, this type of hydrogen-storing alloy is produced by a process which utilizes single substance of Zr or V as the starting material. More specifically, the single substance of the metal as one of the starting material is placed at a predetermined atomic ratio in an aluminum crucible or a water-cooled copper crucible and is directly melted to synthesize the hydrogen-storing alloy in the crucible by placing the crucible in a high-frequency induction heating surface, high-temperature resistance heating oven or an arc melting surface.

When single substance of Zr or V is molten as one of the starting materials, the alloy composition tends to deviate from the expected composition due to such reason that such substance in molten state reacts with the metal of the crucible or due to difference in vapor pressure of such substance from those of other elements at high temperature. It is therefore difficult to obtain homogeneous excellent alloy having the aimed composition. In addition, production of single substance of Zr or V requires a complicated refining process so that the prices of such substances are relatively high. Furthermore, handling of such substances has to be conducted with care to ensure safety, because these single substances generate toxic vapors. Thus, from the view points of practicality, economy and safety, it has been desired that no single substance of Zr or V is used in the production of Zr- or V-type alloys.

Hydrogen-storing alloys produced by processes which do not rely upon single substance of Zr or V are practical in view of both characteristics and cost and, hence, are expected to be promising as materials of electrodes of nickel-hydrogen storage batteries.

Disclosure of the Invention

An object of the present invention is to provide a hydrogen-storing alloy which can be produced at low cost with high degrees of reliability and reproducibility and which exhibits superior hydrogenation characteristics, as well as a storage battery electrode making use of the alloy, thereby overcoming the above-described problems encountered with the production of Zr- or V-containing hydrogen storing alloy.

The production method according to the present invention makes use of commercially available ferrozirconium (Zr-Fe) alloy and zircalloy (Zr-Sn alloy) in place of single substance of Zr and ferrovanadium in place of single substance of vanadium, whereby a hydrogen-storing alloy can be produced with reduced material and production costs, high efficiency, reliability and safety in the production. The thus produced hydrogen-storing alloy is homogeneous without segregation and, therefore, is excellent in properties such as hydrogen storage capacity, reaction speed, electrochemical hydrogen storage/release characteristics in an electrolyte, electrode reaction efficiency, and so forth.

When ferrozirconium, zircalloy and ferrovanadium cannot provide exactly an aimed alloy composition, the present invention does not exclude the use of single substance of the metals so as to adjust the composition thereby enabling production of an alloy exactly having the aimed composition, thus attaining an equivalent effect. The method of the invention provides a stable quality of the product without substantial

fluctuation between lots, as well as high degree of homogeneity of the product alloy, while ensuring high reproducibility of storage and discharge of hydrogen, as well as reliability. Furthermore, the costs are reduced and occurrence of toxic vapors is prevented. It is also to be pointed out that the product alloy exhibits superior anti-oxidation characteristics.

- 5 The present invention is effective when applied to the production of a hydrogen-storing alloy, in particular to an alloy expressed by a general formula $AB\alpha$ [where, A represents one kind selected from the group consisting of: a single substance of Zr; a single substance of Ti; and Zr and at least one selected from the group consisting of Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Pr, Mm, Nb, Nd, Mo, Al and Si. B represents one kind selected from the group consisting of: a single substance of Fe; Fe, V and at least one selected from the group consisting of Ni, Cr, Mn, Co, Cu, Zn, Al, Si, Nb, Mo, W, Mg, Ca, Y, Ta, Pd, Ag, Au, Cd, In, Sn, Bi, La, Ce, Pr, Nd, Th, Sm and Mm (Me represents a mixture of rare earth elements); and Fe and at least one selected from the group consisting of Ni, Cr, Mn, Co, Cu, Zn, Al, Si, Nb, Mo, W, Mg, Ca, Y, Ta, Pd, Ag, Au, Cd, In, Sn, Bi, La, Ce, Pr, Nd, Th, Sm and Mm. α represents a value of from 1.5 to 2.5. A and B are elements different each other or of different compositions. Alternatively, B represents one kind selected from the group consisting of: a single substance of Sn; and Sn and at least one selected from the group consisting of V, Ni, Cr, Mn, Co, Cu, Zn, Al, Si, Nb, Mo, W, Mg, Ca, Y, Ta, Pd, Ag, Au, Cd, In, Bi, La, Ce, Pr, Nd, Th, Sm and Mm (Mm represents a mixture of rare earth elements); α being a value of from 1.5 to 2.5; A and B being different elements each other or of different compositions], wherein the alloy phase substantially belongs to Laves phase of inter-metallic compound with a crystalline structure of hexagon-symmetrical C14 type having crystalline lattice constants of $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type having crystalline lattice constant of $a = 6.92$ to 7.70 .

The advantage of the invention is remarkable particularly also when the alloy produced by the above-described method is used as the material of a hydrogen-storing electrode of a Ni-hydrogen storage battery.

25

Brief Description of the Drawings

- Fig. 1 is a diagram showing discharge cycle life characteristic of half cells having hydrogen-storing electrodes as an embodiment of the present invention; and
- 30 Fig. 2 is a diagram showing discharge cycle life characteristic of batteries having negative electrodes made of various examples of the alloy produced by the method of the present invention.

The Best Mode for Carrying Out the Invention

- 15 In the drawings showing examples of the invention, the number (No.) of batteries represents that the alloy of the corresponding No. in Tables in the specification is used as the electrode material. (Example 1)
- Table 1 shows compositions and price ratio of a single substance of zirconium (Zr) and ferrozirconium alloys which are used as starting materials in the method of the present invention. As will be seen from Table 1, single substance of zirconium metal has a price per unit weight which is about 2 to 7 times as high that of ferrozirconiums. For instance, the ferrozirconium 1 shown in Table 1 is about 1/5 in price as compared with pure Zr and has a Zr content of as high as 80%.

45

50

55

Table 1

	Zr (%, Min.)	Fe (%, Max.)	Mn (%, Max.)	C (%, Max.)	Price ratio to unit weight of Zr
Zirconium 1 (sponge)	99.8	0.03	0.005	0.01	1
Zirconium 2 (sponge)	99.5	0.1	0.01	0.03	0.61
Zirconium 3 (sponge)	99.0	0.5	0.03	0.05	0.52
Ferro- zirconium 1	80.0	19.5	0.2	0.1	0.22
Ferro- zirconium 2	50.0	49.2	0.3	0.1	0.15

Examination by an SEM and a TEM showed that both the-ferrozirconiums 1 and 2 have high degree of homogeneity. It was also found that the vapor pressure of these ferrozirconiums in a molten state is about 1/2 or less that of single substance of Zr, suggesting that deviation of the product composition can be made smaller.

In a conventional method for producing an alloy containing Zr and Fe, in particular alloy of AB α type alloy of Laves phase, materials such as electrolytic iron, mond nickel and so forth are added to the expensive zirconium at predetermined rations and the mixture thus obtained were directly melted to form the alloy. Thus, the conventional process is costly and requires a complicated production process, while posing problems such as easy oxidation of single substance of zirconium and lack of uniformity of the product alloy structure. These problems, however, can be overcome by the use of ferrozirconiums of the type shown in Table 1.

The production method of the invention which makes use of a ferrozirconium can be carried out by the same procedure as that of a known melting process which employs a high-frequency melting furnace or an arc furnace. Zr(Ti)-Fe type alloys of Nos. 1 to 5 shown in Table 5 were mixed at desired composition ratios and melted to form alloys. Each of these alloys exhibited higher degree of homogeneity than prior art alloys, without causing any segregation. In addition, there was no substantial deviation of composition from aimed composition. Fluctuation between lots also was confirmed to be small. Hydrogen storing characteristics such as hydrogen storage capacity, reaction speed and flammability in the air were examined and shown in the same Table. It will be seen that these alloys showed large values of hydrogen storage capacities and excellent properties such as reaction speed. (Example 2)

Alloys of compositions of Nos. 6 to 11 shown in Table 2 were prepared through the same process as Example 1 by selecting, among AB α type alloys, alloys expressed by a general formula of Zr α Ni γ M δ , [where α , γ and δ represent atomic rations of Zr, Ni and M satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Fe; and Fe and at least one selected from the group consisting of V, Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm], which Zr α Ni γ M δ alloys were produced by using, as the starting materials, commercially available ferrozirconiums and other elements selected from the group consisting of Zr, Ni, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Mm, Nb, Nd, Sm, Mo, Al, Si, V, Cr, Mn, Fe, Co, Cu, Zn, Si, Nb, Mo, W and Cd.

Table 2

Alloy No.	Alloy Composition	Hydrogen-Storage Capacity (ml/g)
1	ZrFe	186
2	ZrFe _{1.25} V _{0.3}	245
3	Zr _{1.2} Fe _{0.2} Mn _{0.4} Al _{0.1}	211
4	Zr _{0.6} Ti _{0.4} Fe _{0.6} V _{0.8}	238

5	ZrCo _{1.0} Fe _{0.3} Mn _{0.3}	268
6	ZrV _{0.2} Ni _{1.4} Fe _{0.4}	2-2
7	ZrV _{0.3} Ni _{1.3} Fe _{0.2}	218
8	Zr _{1.1} Hf _{0.1} V _{0.6} Ni _{1.2} Fe _{0.2}	207
9	Zr _{0.6} V _{0.7} Ni _{1.2} Fe _{0.7} Mn _{0.2}	205
10	ZrV _{0.4} Ni _{1.8} Fe _{0.3} Mn _{0.3}	219
11	ZrV _{0.2} Ni _{1.3} Ce _{0.1} Co _{0.1} Fe _{0.2}	200
12	ZrV _{0.2} Ni _{1.4} Fe _{0.4}	154
13	Ti _{0.3} Zr _{0.7} V _{0.4} Ni _{1.0} Fe _{0.4}	149
14	Zr _{0.4} V _{0.3} Ni _{1.0} Fe _{0.5}	98
15	ZrV _{0.5} Ni _{1.3} Fe _{1.9}	112

More specifically, the ferrozirconium and other materials were weight and mixed to provide the compositions shown in Table 2 and were directly melted in an argon-arc melting furnace (or by a high-frequency induction heating furnace maintaining argon or other inert gas atmosphere). Part of each of alloys thus obtained was used for alloy analysis for examining atomic composition, crystalline structure, crystalline lattice constants and homogeneity, while the remainder was used for measurement of hydrogen storage/release characteristics conducted in hydrogen gas [mainly with respect to the measurement of P (pressure), C (composition) and T (temperature)] as well as for evaluation of electrochemical performance.

As results of the analysis, it was confirmed that each of the alloys Nos. 6 to 11 had homogeneous structure with alloy phases of C14 or C15 type Laves phase. The crystalline lattice constants thereof were $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 in a case of type C14 which was hexagonal symmetric phase and other crystalline lattice constants were $a = 6.92$ to 7.70 in a case of the type C15 which was cubic symmetrical phase. It was confirmed also that there was no substantial deviation of composition. Hydrogen storage capacities of these alloys were measured from ordinary P-C-T characteristics to obtain the results shown in Table 2. It will be seen that the storage capacities are greater than those of prior art alloys. Other characteristics such as reaction speed also were found to be excellent.

Alloys produced by conventional production methods are also shown as Nos. 12 to 15 for the purpose of comparison. These alloys showed inferior homogeneity and deviation of composition, and considerably smaller values of hydrogen storage capacity though these comparison alloys were of similar type to that of the alloys produced by the method of the invention.

5 Many alloy compositions are obtainable by the production method of the invention in addition to those shown in Table 2. Hydrogen-storing electrodes were produced with those obtainable alloys but specifically remarkable effect was attained with the alloys having alloy phases substantially belongs to Laves phase of intermetallic compound with a crystalline structure of hexagon-symmetrical C14 type having crystalline lattice constants of $a = 4.8$ to 2.5 and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type having crystalline
10 lattice constant of $a = 6.92$ to 7.70 .

Thus, the method of the invention for producing a hydrogen-storing alloy from a ferrozirconium containing Fe and Zr as the starting material was confirmed to be simpler than known methods and to be able to provide remarkably higher degree of homogeneity, as well as superior hydrogen storage, holding and transportation characteristics, as compared with alloys produced by conventional method which
15 employed single substances of Fe and Zr as the starting materials.

The present inventors compared and evaluated the alloys produced by the method of the invention from the viewpoint of hydrogen storage/release capacity, in order to find the optimum composition.

As a result, the inventors have found that the best results are obtained when the alloy composition falls within a range which is expressed by a general formula of $Zr\alpha Ni\gamma M\delta$, [where α , γ and δ represent atomic ratios of Zr, Ni and M, satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Fe; and
20 Fe and at least one selected from the group consisting of V, Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm].

Alloys having the atomic ratio δ smaller than 0.01 or greater than 1.8 equally showed somewhat small
25 values of hydrogen release amounts. Alloys having atomic ratio α smaller than 0.5 showed somewhat inferior hydrogen storage capacity, while Alloys having atomic ratio α greater than 1.5 showed comparatively small value of hydrogen release amount. Alloys having atomic ratio γ smaller than 0.4 showed inferior durability against repetition of hydrogen storage/release cycles, while alloys having atomic ratio γ greater than 2.5 showed somewhat small value of hydrogen storage capacity. Alloys with values $(\gamma + \delta)$ smaller
30 than 1.2 and greater than 3.7 respectively showed rather inferior hydrogen release amounts and rather inferior hydrogen storage capacities. The reasons of these facts are shown below. The Zr content α is a factor which affects particularly the hydrogen storage capacity. The greater the Zr content, the greater the hydrogen storage capacity. Zr, however, forms a stable hydrogen compound and, therefore, exhibits a smaller hydrogen release rate and, hence, smaller hydrogen release amount. The Ni content is a factor
35 which affects particularly the storage/release cycle (durability). The greater the Ni content, the longer the life. A too large Ni content, however, tends to reduce hydrogen release capacity. The content δ of M relates specifically to the storage/release cycle and the discharge pressure. Both the storage/release cycle and the release pressure were improved by an increase in the M content, but the hydrogen storage capacity was reduced as a result of the increase in the M content. It was also confirmed that the use of Fe as an
40 essential element provides higher meltability and homogeneity of alloys, as well as industrial and economical advantages due to its low price.

Hydrogen-storing negative electrodes of alkali storage battery were produced by the alloys of the invention. The alloys having a composition expressed by the above-mentioned general formula of $Zr\alpha Ni\gamma M\delta$ showed specifically large electric storage capacity values, as shown in Table 3.

Table 3

Alloy No.	Alloy Composition	Amount of discharge after 10 cycles (mAh/g)
16	$\text{ZrNi}_{1.4}\text{Fe}_{0.6}$	346
17	$\text{ZrNi}_{1.3}\text{Fe}_{0.25}\text{V}_{0.3}$	345
18	$\text{Zr}_{1.2}\text{Ni}_{1.2}\text{Fe}_{0.2}\text{Mn}_{0.5}$	341
19	$\text{Zr}_{0.6}\text{Ni}_{1.2}\text{Fe}_{0.6}\text{V}_{0.8}$	338

20	$\text{ZrNi}_{1.0}\text{Fe}_{0.3}\text{Mn}_{0.3}$	368
21	$\text{ZrNi}_{1.3}\text{Ce}_{0.1}\text{Co}_{0.1}\text{Fe}_{0.2}$	338

(Example 3)

Table 4 shows compositions and price ratio of a single substance of zirconium (Zr) and zircalloys which are used as starting materials in the method of the present invention. As will be seen from Table 4, single substance of zirconium metal has a price per unit weight which is about 3 to 8 times as high that of zircalloys. For instance, the zircalloy 1 shown in Table 1 is about 1/7 in price as compared with pure Zr and yet the Zr content is as high as 98%.

Table 4

	Zr (%, Min.)	Sn (%, Max.)	Fe (%, Max.)	Cr (%, Max.)	Price ratio to unit weight of Zr
Zirconium 1 (sponge)	99.8	0.005	0.03	0.05	1
Zirconium 2 (sponge)	99.5	0.01	0.1	0.07	0.61
Zirconium 3 (sponge)	99.0	0.04	0.5	0.17	0.52
Zircalloy 1 (bulk)	98.1	1.4	0.1	0.1	0.15
Zircalloy 2 (bulk)	90.0	5.2	1.4	1.2	0.12

Further, the examination thereof showed that both the zircalloys 1 and 2 have high degree of homogeneity. It was also found that the vapor pressure of these zircalloys when molten is lower than that of single substance of Zr, suggesting that deviation of the product composition can be made smaller.

In the conventional method for producing an alloy containing Zr and Sn, in particular alloys of AB α type alloy of Laves phase, materials such as electrolytic iron, mond nickel, single substance of Sn and so forth are added to the expensive zirconium at a predetermined ratio and the mixture thus obtained were directly melted to form the alloy. Thus, the conventional process is high in cost and requires a complicated production process, while posing problems such as easy oxidation of single substance of zirconium and lack of uniformity of the product alloy structure. These problems, however, can be overcome by the use of zircalloys of the type shown in Table 4.

The production method of the invention which makes use of a zircalloy can be carried out by the same procedure as that of a known melting process which employs a high-frequency melting furnace or an arc furnace. Zr(Ti)-M type alloys (M being Sn and at least one selected from the group consisting of Fe, V, Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Bi, La, Ce, Mm, Pr, Nd, Th and Sm) of Nos. 22 to 26 shown in Table 5 were dispensed at desired composition ratios and melted to form alloys. Each of these alloys exhibited higher degree of homogeneity than prior art alloys, without suffering any segregation. In addition, there was no substantial deviation of composition from aimed composition. Fluctuation between lots also as confirmed to be small. Hydrogen storing characteristics such as hydrogen storage capacity, reaction speed and flammability in the air were examined and shown in the same Table. It will be seen that these alloys showed large values of hydrogen storage capacity and excellent properties such as reaction speed. (Example 4)

Alloys of compositions of Nos. 27 to 32 shown in Table 5 were prepared by the same process as example 3, selecting, among AB α type alloys, alloys expressed by a general formula of Zr α Ni γ M δ , [where α , γ and δ represent atomic ratios of Zr, Ni and M, satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Sn; and Sn and at least one selected from the group consisting of Fe, V, Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Bi, La, Ce, Mm, Pr, Nd, Th and Sm], using as the starting materials, commercially available zircalloys and other elements such as Zr, Ni, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Mm, Nb, Nd, Sm, Mo, Al, Si, V, Cr, Mn, Fe, Co, Cu, Zn, Si, Nb, Mo, W and Cd.

Table 5

Alloy No.	Alloy Composition	Hydrogen-Storage Capacity (ml/g)
22	ZrSn _{0.05}	384
23	ZrSn _{0.25} V _{1.3}	345
24	Zr _{1.2} Sn _{0.2} Mn _{0.4} Al _{0.1}	351
25	Zr _{0.6} Ti _{0.6} Sn _{0.6} V _{0.8}	337
26	ZrSn _{0.3} Co _{1.0} Fe _{0.3}	328
27	ZrSn _{0.3} V _{0.2} Ni _{1.4}	252
28	ZrSn _{0.1} V _{0.3} Ni _{1.3} Fe _{0.2}	226
29	Zr _{1.1} Hf _{0.1} Sn _{0.2} V _{0.6} Ni _{1.2}	241
30	Zr _{0.6} Ti _{0.3} Sn _{0.3} Ni _{1.5} Mn _{0.2}	219
31	ZrSn _{0.1} V _{0.4} Ni _{1.2} Mn _{0.3}	204
32	ZrSn _{0.2} Ni _{1.3} Ce _{0.1} Co _{0.4}	223
33	ZrSn _{0.1} V _{0.3} Ni _{1.5}	162
34	Zr _{0.7} Ti _{0.3} Sn _{0.3} V _{0.7} Ni _{1.0}	150
35	ZrSn _{0.2} V _{0.3} Ni _{1.2} Fe _{0.2}	135
36	ZrSn _{0.5} Ni _{1.3} Fe _{1.9}	122

More specifically, zircalloys and other materials were weighed and mixed to provide the compositions shown in Table 5 and were directly melted in an argon-arc melting furnace (or by a high-frequency induction heating furnace maintaining argon or other inert gas atmosphere). Analysis and evaluation methods are the same as that explained in connection with ferrozirconium.

As results of the analysis, it was confirmed that each of the alloys Nos. 27 to 32 shown in Table 5 had homogeneous structure with alloy phases of C14 or C15 type Laves phase. The crystalline lattice constants were $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 in a case of type C14 which was hexagonal symmetric phase and the crystalline lattice constant were $a = 6.92$ to 7.70 in another case of the type C15 which was cubic symmetrical phase. It was confirmed also that there was no substantial deviation of composition. Hydrogen storage capacities of these alloys were measured from ordinary P-C-T characteristics to obtain the results shown in Table 5. It will be seen that the storage capacities are greater than those of known alloys. Other characteristics such as reaction speed also were found to be excellent.

Alloys produced by conventional production methods are also shown in Table 5 as Nos. 33 to 36 for the purpose of comparison. These alloys showed inferior homogeneity and deviation of composition, and considerably smaller values of hydrogen storage capacity though these comparison alloys were of similar type to that of the alloys produced by the method of the invention.

Many alloy compositions are obtainable by the production method of the invention in addition to those shown in Table 5. Hydrogen-storing electrodes were produced with those obtainable alloys but specifically

Table 6

Alloy No.	Alloy Composition	Amount of Discharge after 10 cycles (mAh/g)
37	ZrSn _{0.4} Ni _{1.6}	334
38	ZrSn _{0.25} Ni _{1.3} V _{0.3}	328
39	Zr _{1.2} Sn _{0.2} Ni _{1.2} Mn _{0.5}	343
40	Zr _{0.9} Sn _{0.1} Ni _{1.2} Fe _{0.3} V _{0.8}	326
41	ZrSn _{0.3} Ni _{1.2} Cr _{0.3}	337
42	ZrSn _{0.2} Ni _{1.3} Ce _{0.1} Co _{0.1}	312

(Example 5)

Table 7 shows compositions and price ratio of a single substance of vanadium (V) and ferrovanadium alloys which were used as starting materials in the method of the present invention. As will be seen from Table 1, single substance of vanadium metal has a price per unit weight which is about 3 to 4 times as high that of ferrovanadium. For instance, the ferrovanadium 1 shown in Table 7 is about 1/3 in price as compared with pure vanadium and yet the vanadium content is as high as 70%.

Table 7

	V (% min.)	Fe (% Max.)	Mn (% Max.)	C (% Max.)	Price ratio to unit weight of V
Vanadium 1 (Flake)	99.8	0.03	0.002	0.01	1
Vanadium 2 (Flake)	99.5	0.1	0.01	0.03	0.71
Vanadium 3 (Flake)	99.0	0.5	0.03	0.05	0.62
Ferro- vanadium 1	70.00	29.3	0.2	0.1	0.32
Ferro- vanadium 2	40.0	59.2	0.3	0.1	0.25

Examination showed that both the ferrovanadiums 1 and 2 have high degree of homogeneity. It was also found that the vapor pressure of these ferrovanadium when melted is about 1/2 or less that of single substance of V, suggesting that deviation of the product composition can be made smaller.

remarkable effect was attained with alloys having a composition expressed by a general formula $AB\alpha$ - [where, A represents at least one selected from the group consisting of Zr, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Pr, Mm, Nb, Nd, Mo, Al and Si and B represents one kind selected from the group consisting of: a single substance of Sn; and Sn and at least one selected from the group consisting of Fe, V, Ni, Cr, Mn, Co, Cu, Zn, Al, Si, Nb, Mo, W, Mg, Ca, Y, Ta, Pd, Ag, Au, Cd, In, Bi, La, Ce, Pr, Nd, Th, Sm and Mm (Mm represents a mixture of rare earth elements); α represents a value of 1.5 to 2.5, and A and B are different elements], wherein the alloy phase substantially belongs to Laves phase of intermetallic compound with a crystalline structure of hexagon-symmetrical C14 type with crystalline lattice constants of $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type with crystalline lattice constant of $a = 6.92$ to 7.70 . Further, regarding the cubic-symmetrical C15 type, alloys having crystalline lattice constant of 6.92 to 7.70 particularly exhibited excellent characteristics.

Thus, the method of the invention for producing a hydrogen-storing alloy from a zircalloy containing Zr and Sn as the starting material was confirmed to be simpler than known methods and to be able to provide much higher degree of homogeneity, as well as hydrogen storage, holding and transportation characteristics, as compared with alloys produced by conventional method which employed single substances of Fe and Zr as the starting materials.

The present inventors compared and evaluated the alloys produced by the method of the invention from the viewpoint of hydrogen storage/release capacity, in order to find the optimum composition, as in the case of the ferrozirconium alloy (Zr-Fe alloy) explained before.

As a result, the inventors have found that the best results are obtained when the alloy composition falls within a range which is expressed by a general formula of $Zr\alpha Ni\gamma M\delta$, [where α , γ and δ represent atomic ratios of Zr, Ni and M, satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Sn; and Sn and at least one selected from the group consisting of Fe, V, Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Bi, La, Ce, Mm, Pr, Nd, Th and Sm].

Alloys having the atomic ratio δ smaller than 0.01 or greater than 1.8 showed somewhat small values of hydrogen release amounts. Alloys having atomic ratio α smaller than 0.5 showed somewhat inferior hydrogen storage capacity, while Alloys having atomic ratio α greater than 1.5 showed comparatively small value of hydrogen release amount. Alloys having atomic ratio γ smaller than 0.4 showed inferior durability against repetition of hydrogen storage/release cycles, while alloys having atomic ratio γ greater than 2.5 showed somewhat small value of hydrogen storage capacity. Alloys with values $(\gamma + \delta)$ smaller than 1.2 and greater than 3.7 respectively showed rather inferior hydrogen release amounts and rather inferior hydrogen storage capacities. The reasons of these facts are shown below. The Zr content α is a factor which affects particularly the hydrogen storage capacity. The greater the Zr content, the greater the hydrogen storage capacity. Zr, however, forms a stable hydrogen compound and, therefore, exhibits a smaller hydrogen release rate and, hence, smaller hydrogen release amount. The Ni content is a factor which affects particularly the storage/release cycle (durability). The greater the Ni content, the longer the life. A too large Ni content, however, tends to reduce hydrogen storage capacity. The content δ of M relates specifically to the storage/release cycle and the discharge pressure. Both the storage/release cycle and the release pressure were improved by an increase in the M content, but the hydrogen storage capacity was reduced as a result of the increase in the M content. It was also confirmed that the use of Sn as an essential element provides higher meltability and homogeneity of alloys, as well as industrial and economical advantages due to its low price.

Hydrogen-storing negative electrodes of alkali storage battery were produced by the alloys of the invention. The alloys having a composition expressed by the above-mentioned general formula of $Zr\alpha Ni\gamma M\delta$ showed specifically large electric storage capacity values.

In the conventional method for producing an alloy containing in and Fe, in particular alloy of AB α type alloy of Lavas phase, materials such as electrolytic iron, mond nickel and so forth are added to the expensive vanadium at predetermined ratio and the mixture thus obtained were directly melted to form the alloy. Thus, the conventional process is costly and requires a complicated production process, while posing problems such as toxicity of single substance of V and lack of uniformity of the product alloy structure. These problems, however, can be overcome by the use of ferrovanadiums of the type shown in table 7.

The production method of the invention which makes use of a ferrovanadium can be carried out by the same procedure as that of a known melting process which employs a high-frequency melting furnace of an arc furnace. Ti(Zr)-Ni type alloys, Fe-V type alloys and Ti(Zr)-V type alloys of Nos. 43 to 47 shown in Table 8 were dispensed at desired composition ratios and melted to form alloys. Each of these alloys exhibited higher degree of homogeneity than prior art alloys, without suffering any segregation. In addition, there was no substantial deviation of composition from aimed composition. Fluctuation between lots also was confirmed to be small. Hydrogen storing characteristics such as hydrogen storage capacity, reaction speed and flammability in the air were examined and shown in the same Table. it will be seen that these alloys showed large values of hydrogen storage capacities and excellent properties such as reaction speed. (Example 6)

Alloys of compositions of Nos. 48 to 53 shown in Table 8 were prepared by the same process as Example 1, selecting, among AB α type alloys, alloys expressed by a general formula of Zr α V β Ni γ M δ , [where α , β , γ and δ represent atomic ratios of Zr, V, Ni and M satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\beta = 0.01$ to 1.2 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\beta + \gamma + \delta = 1.2$ to 3.7 , while m represents one selected from the group consisting of: a single substance of Fe; and Fe and at least one selected from the group consisting of Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm], using, as the starting materials, commercially available ferrovanadiums and other elements such as Zr, Ni, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Mm, Nb, Nd, Sm, Mo, Al, Si, V, Cr, Mn, Fe, Co, Cu, Zn, Si, Nb, Mo, W and Cd.

Table 8

Alloy No.	Alloy Composition	Amount of discharge after 10 cycles (mAh/g)
43	FeV	177
44	TiFe _{1.2} V _{0.8}	181
45	ZrV _{1.5} Fe _{0.5}	243
46	Ti _{0.5} Zr _{0.5} V _{1.2} Fe _{0.8}	218
47	FeV _{1.0} Mn _{0.5} Co _{0.5}	162
48	ZrV _{0.2} Ni _{1.4} Fe _{0.4}	202
49	ZrV _{0.3} Ni _{1.3} Fe _{0.2}	218

50	$\text{Zr}_{1.2}\text{V}_{0.6}\text{Ni}_{1.2}\text{Fe}_{0.2}$	207
51	$\text{Zr}_{0.6}\text{V}_{0.9}\text{Ni}_{1.2}\text{Fe}_{0.7}$	205
52	$\text{ZrV}_{0.4}\text{Ni}_{1.0}\text{Fe}_{0.3}\text{Mn}_{0.3}$	219
53	$\text{ZrV}_{1.0}\text{Ni}_{1.3}\text{Ce}_{0.1}\text{Co}_{0.1}\text{Fe}_{0.2}$	200
54	$\text{ZrV}_{0.2}\text{Ni}_{1.4}\text{Fe}_{0.4}$	141
55	$\text{TiV}_{0.4}\text{Ni}_{1.0}\text{Fe}_{0.3}\text{Mn}_{0.3}$	146
56	$\text{Zr}_{0.4}\text{V}_{0.3}\text{Ni}_{1.0}\text{Fe}_{0.5}$	84
57	$\text{ZrV}_{0.1}\text{Ni}_{1.3}\text{Fe}_{1.9}$	108

More specifically, ferrovanadiums and other materials were weighed and mixed to provide the compositions shown in Table 8 and were directly melted in an argon-arc melting furnace to form alloys. Hydrogen storage capacities of these alloys were measured from ordinary P-C-T characteristics to obtain the results shown in Table 8. It will be seen that the storage capacities are greater than those of prior art alloys. Other characteristics such as reaction speed also were found to be excellent.

Alloys produced by conventional production methods are also shown as Nos. 54 to 57 for the purpose of comparison. These alloys showed inferior homogeneity and deviation of composition, and considerably smaller values of hydrogen storage capacity as shown in Table 9, though these comparison alloys were of similar type to that of the alloys produced by the method of the invention.

Thus, the method of the invention for producing a hydrogen-storing alloy from a ferrovanadium containing Fe and V as the starting material was confirmed to be simpler than prior art methods and to be able to provide much higher degree of homogeneity, as well as superior hydrogen storage, holding and transportation characteristics, as compared with alloys produced by conventional method which employed single substances of Fe and V as the starting materials.

The present inventors compared and evaluated the alloys produced by the method of the invention from the viewpoint of hydrogen storage/release capacity, in order to find the optimum composition.

As a result, the inventors have found that the best results are obtained when the alloy composition falls within a range which is expressed by a general formula of $\text{Zr}_\alpha\text{V}_\beta\text{Ni}_\gamma\text{M}_\delta$, [where α , β , γ and δ represent atomic ratios of Zr, V, Ni and M, satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\beta = 0.03$ to 1.2 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\beta + \gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Fe; and Fe and at least one selected from the group consisting of Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Zl, Si, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm].

Alloys having the atomic ratio β smaller than 0.01 or greater than 1.2 showed rather small amount of release of hydrogen, though considerably large values of hydrogen storage capacity were observed. Alloys having the atomic ratio δ smaller than 0.01 or greater than 1.8 showed somewhat small values of hydrogen release amounts. Alloys having atomic ratio α smaller than 0.5 showed somewhat inferior hydrogen storage capacity, while Alloys having atomic ratio α smaller than 0.5 showed somewhat inferior hydrogen storage capacity, while Alloys having atomic ratio α greater than 1.5 showed comparatively small value of hydrogen release amount. Alloys having atomic ratio γ smaller than 0.4 showed inferior durability against repetition of hydrogen storage/release cycles, while alloys having atomic ratio γ greater than 2.5 showed somewhat small value of hydrogen storage capacity. Alloys with values $(\beta + \gamma + \delta)$ smaller than 1.2 or greater than 3.7 respectively showed rather inferior hydrogen release amounts and rather inferior hydrogen storage capacities. The reasons of these facts are shown below. The Zr content α and the V content β are factors which affect particularly the hydrogen storage capacity. The greater the Zr and V contents, the greater the hydrogen storage capacity. Zr and V, however, form stable hydrogen compounds and, therefore, exhibits a smaller hydrogen release rate and, hence, smaller hydrogen release amount. The Ni content is a factor which affects particularly the storage/release cycle (durability). The greater the Ni contents the longer the life. A too large Ni content, however, tends to reduce hydrogen storage capacity. The content δ of M relates

specifically to the storage/release cycle and the release pressure. Both the storage/release cycle and the release pressure were improved by an increase in the M content, but the hydrogen storage capacity was reduced as a result of the increase in the M content. It was also confirmed that the use of Fe as an essential element provides higher meltability and homogeneity of alloys, as well as industrial and economical advantages due to its low price. (Example 7)

Alloys of compositions of shown in Table 9 were prepared by selecting, among AB α type alloys, alloys expressed by a general formula of Zr α V β Ni γ M δ , [where α , β , γ and δ represent atomic ratios of Zr, V, Ni and M, satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\beta = 0.01$ to 1.2 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\beta + \gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Fe; and Fe and at least one selected from the group consisting of Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm], using, as the starting materials, commercially available ferrovanadiums and other elements such as Zr, Ni, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Mm, Nb, Nd, Sm, Mo, Al, Si, V, Cr, Mn, Fe, Co, Cu, Zn, Si, Nb, Mo, W and Cd.

As a result of analysis, it was found that the alloys Nos. 58 to 63 among the alloys shown in Table 9 have main alloy phases of C14 or C15 Laves phase. These alloys showed almost no deviation of composition. Furthermore, these alloys showed greater values of hydrogen storage capacity than conventional alloys when evaluated through measurement of ordinary P-C-T characteristics with hydrogen gas. Characteristics such as reaction speed and equilibrium pressure hysteresis also were found to be superior.

Alloys Nos. 64 to 68 are conventional alloys used as materials of hydrogen-storing electrodes. These alloys do not meet the requirements of the invention: namely, the alloys phases of these comparison sample alloys did not belong to Laves phase of intermetallic compound with a crystalline structure of hexagon-symmetrical C14 type with crystalline lattice constants of $a = 4.8$ to 5.2 Å (Angstrom) and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type with crystalline lattice constant of $a = 6.92$ to 7.70 . More specifically, the alloy No. 64 had a too large atomic ratio of V, the alloy No. 65 had a too small atomic ratio of Zr, the alloy No. 66 had a too small atomic ratio of Ni and the alloy No. 67 had a too large atomic ratio of M. The alloy No. 68 had the same alloy composition as the alloy No. 58 but was prepared by a process which did not use ferrovanadium.

Performance of these alloys, when used as negative electrodes of alkali storage batteries, were evaluated through semi-battery test of the negative electrodes. The evaluation method and the results are shown in Fig. 1, as well as in the following description.

Each alloy produced by melting was pulverized into particles of particle size below 300 meshes. 5 g of this particulated alloy was mixed with 0.5 g of polyethylene powder as the binder and 2 g of carbonyl nickel as a conducting agent. The mixture was sufficiently stirred and blended and was applied around a nickel mesh (wire diameter 0.2 mm, 16 mesh) which was used as a core conductor, and was then pressed into a tabular form. The alloy in the tabular form was heated at 120°C in a vacuum so as to melt and remove polyethylene, and then a lead was connected to the tabular alloy thus completing a hydrogen-storing alloy.

In order to evaluate the performance of the alloy as the negative electrode of a secondary battery, sintered nickel plates used in commercially available nickel-cadmium battery were used as positive electrodes (opposite electrodes) and were combined with the hydrogen-storing alloy negative electrodes such that the amounts of the positive electrodes were excess of those of the negative electrodes in terms of electricity capacity. Batteries were formed with those pairs of electrodes, using non-woven polyamide cloths as separators and using an electrolyte which was prepared by adding 20 g/l of lithium hydroxide to an aqueous solution of caustic potash having a specific gravity of 1.30. The batteries were subjected to repeated charging and discharging with constant electrical current at 20°C . The amount of electricity charged was 500 mA x 5 hours, while discharge was conducted at 30 mA with a voltage below 0.8 V being cut.

Table 9 shows the discharge capacitances in the open systems as observed in 10th charging/discharging cycles, while Fig. 1 shows the charging/discharging cycle life characteristics. More specifically, in Fig. 1, the axis of abscissa represents the number (∞) of the charging/discharging cycles, while axis of ordinate represents the discharging capacity per 1 g in the open system as observed in the batteries having negative electrodes made of alloys of the invention, together with the characteristics obtained with unacceptable alloys (Table 9). The numbers (Nos.) allocated to the batteries shown in Fig. 1 correspond to the Nos. of alloys shown in Table 9. From the comparison between the alloy No. 58 and the alloy No. 68, as well as from the comparison between the alloys Nos. 58 to 63 and the alloys Nos. 64 to 67, it will be seen that the hydrogen-storing alloys of the present invention have greater values of discharge capacities, as well as superior durability (cycle life characteristics), as compared with conventional alloys. Superiority in quick charging/discharging characteristics also was confirmed.

Table 9

Alloy No.	Alloy Composition	Amount of discharge after 10 cycles (mAh/g)
58	$\text{ZrV}_{0.2}\text{Ni}_{1.4}\text{Fe}_{0.4}$	346
59	$\text{ZrV}_{0.3}\text{Ni}_{1.3}\text{Fe}_{0.2}$	355
60	$\text{Zr}_{1.2}\text{V}_{0.6}\text{Ni}_{1.2}\text{Fe}_{0.2}$	344
61	$\text{Zr}_{0.5}\text{V}_{0.9}\text{Ni}_{1.2}\text{Fe}_{0.7}$	328
62	$\text{ZrV}_{0.4}\text{Ni}_{1.0}\text{Fe}_{0.3}\text{Mn}_{0.3}$	358
63	$\text{ZrV}_{0.2}\text{Ni}_{1.3}\text{Ce}_{0.1}\text{Co}_{0.1}\text{Fe}_{0.2}$	338
64	$\text{ZrV}_{1.3}\text{Ni}_{0.9}\text{Fe}_{1.5}$	197
65	$\text{Zr}_{0.4}\text{V}_{0.3}\text{Ni}_{1.0}\text{Fe}_{0.5}$	144
66	$\text{ZrV}_{0.5}\text{Ni}_{0.3}\text{Fe}_{1.0}$	199
67	$\text{ZrV}_{0.5}\text{Ni}_{1.3}\text{Fe}_{1.9}$	185
68	$\text{ZrV}_{0.2}\text{Ni}_{1.3}\text{Fe}_{0.4}$	298

Many alloy compositions for hydrogen-storing electrodes are obtainable by the production method of the invention in addition to those shown in Table 9. The alloy phases of those alloys substantially belonged to Laves phase of intermetallic compound having a crystalline structure of hexagon-symmetrical C14 type with crystalline lattice constants of $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type with crystalline lattice constant of $a = 6.92$ to 7.70 .

The inventors have found that the best results are obtained when the alloy composition falls within a range which is expressed by a general formula of $\text{Zr}_\alpha\text{V}_\beta\text{Ni}_\gamma\text{M}_\delta$, where α , β , γ and δ represent atomic ratios of Zr, V, Ni and M satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\beta = 0.01$ to 1.2 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\beta + \gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Fe; and Fe and at least one selected from the group consisting of Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm].

Alloys having the atomic ratio β smaller than 0.01 or greater than 1.2 showed rather small amount of release of hydrogen, though considerably large values of hydrogen storage capacity were observed. Alloys having the atomic ratio δ smaller than 0.01 or greater than 1.8 showed somewhat small values of hydrogen release amounts. Alloys having atomic ratio α smaller than 1.5 showed somewhat inferior hydrogen storage capacity, while alloys having atomic ratio α greater than 1.5 showed comparatively small value of hydrogen release amount. Alloys having atomic ratio γ smaller than 0.4 showed inferior durability against repetition of hydrogen storage/release cycles, while alloys having atomic ratio γ greater than 2.5 showed somewhat small value of hydrogen storage capacity. Alloys with values $(\beta + \gamma + \delta)$ smaller than 1.2 or greater than 3.7 respectively showed rather inferior hydrogen release amounts and rather inferior hydrogen storage capacities. The reasons of these facts are shown below. The Zr content α and the V content β are factors which affect particularly the hydrogen storage capacity. The greater the Zr and V contents, the greater the hydrogen storage capacity. Zr and V, however, form stable hydrogen compounds and, therefore, exhibits a smaller hydrogen release rate and, hence, smaller hydrogen release amount. The Ni content is a factor which affects particularly the storage/release cycle (durability). The greater the Ni content, the longer the life. A too large Ni content, however, tends to reduce hydrogen storage capacity. The content δ of M relates

specifically to the storage/release cycle and the release pressure. Both the storage/release cycle and the release pressure were improved by an increase in the M content, but the hydrogen storage capacity was reduced as a result of the increase in the M content. It was also confirmed that the use of Fe as an essential element provides higher meltability and homogeneity of alloys, as well as industrial and economic advantages due to its low price.

The hydrogen-storing alloys, formed by using a ferrovandium containing Fe and V as the starting material, exhibited very high degree of homogeneity, and hydrogen-storing electrodes making use of these alloys as the major component exhibit superior performance when used as negative electrodes of an alkali batteries, as compared with alloys formed by the conventional process which makes use of single substances of Fe and V as the starting materials. (Example 8)

A U2 type cylindrical hermetic nickel-hydrogen secondary batteries were produced using the above-mentioned hydrogen-storing alloy electrodes and thus formed batteries were evaluated. As in the case of the single-electrode test mentioned before, the alloy was pulverized into particles of a particle size below 300 meshes, and was mixed with a binder such as polyvinyl alcohol, whereby a paste was formed. The paste was applied to a punching metal plate plated with nickel and was then dried. The plate was then slitted into strips of 3.9 cm wide and 26 cm long, and lead plates were spot-welded to predetermined portions on the strip thus forming hydrogen-storing alloys. Known foamed nickel electrodes, in the form of strips of 3.9 cm wide and 22 cm long, were used as the opposing electrodes. A polyamide non-woven cloth was used as separators, together with an electrolyte which was formed by adding 20g/l of lithium hydroxide to an aqueous solution of caustic potash having a specific gravity of 1.20. The nominal capacity was 3.0 Ah.

The evaluation was conducted by subjecting these batteries to charging/discharging cycles repeated at 20°C. The charging was conducted for 15 hours at 0.1C (10-hour charging rate), while the discharging was conducted at 0.2C (5-hour discharge rate) until the voltage is reduced to the final voltage of 0.9V. The results of this test are shown in Fig. 2. The Nos. of the batteries appearing in Fig. 2 correspond to the Nos. of alloys shown in Table 2. The batteries incorporating electrodes made of the hydrogen-storing alloys of the invention maintained discharge capacities of about 3.0 to 3.2 Ah and did not show any degradation in the performance even after 500 charging/discharging cycles. Industrial Applicability:

The alloys produced by the method of the present invention, as well as electrodes made from such alloys, exhibit high degrees of homogeneity and reduced fluctuation in quality between lots, thus offering high stability of quality and high reliability. In addition, the price of the alloy is low by virtue of low material cost and simplified production process. Consequently, the present invention provides alloys which are superior in various characteristics such as hydrogen storage/release characteristics and cycle life, as well as oxidation resistance. Thus, the alloys produced by the method of the present invention find various industrial uses such as storage, holding and transportation of hydrogen, elements of a heat pump, elements of alkali batteries (nickel-hydrogen battery) and so forth, thus offering great industrial advantages.

Claims

1. A method of producing a hydrogen-storing alloy, characterized by using, as a starting material, at least a ferrozirconium (Zr-Fe alloy).
2. A method of producing a hydrogen-storing alloy, characterized by using, as a starting material, at least a ferrozirconium (Zr-Fe alloy), wherein said hydrogen-storing alloy is an alloy expressed by a general formula of $AB\alpha$ [where, A represents at least one selected from the group consisting of Zr, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Pr, Mm, Nb, Nd, Mo, Al and Si and B represents one selected from the group consisting of: a single substance of Fe; and Fe and at least one selected from the group consisting of V, Ni, Cr, Mn, Co, Cu, Zn, Al, Si, Nb, Mo, W, Mg, Ca, Y, Ta, Pd, Ag, Au, Cd, In, Sn, Bi, La, Ce, Pr, Nd, Th, Sm and Mm (Mm represents a mixture of rare earth elements); α represents a value of from 1.5 to 2.5, and A and B are different elements], wherein the alloy phase substantially belongs to Laves phase of intermetallic compound with a crystalline structure of hexagon-symmetrical C14 type having crystalline lattice constants of $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type having crystalline lattice constant of $a = 6.92$ to 7.70 .
3. A method of producing a hydrogen-storing alloy according to Claim 1, wherein said alloy or its hydrogenated product contains, as the component A, at least 30 atom % of Zr.

4. A method of producing a hydrogen-storing alloy according to one of Claims 1, 2 and 3, wherein said alloy or its hydrogenated product is expressed by a general formula of $Zr_{\alpha}Ni_{\gamma}M_{\delta}$, [where α , γ δ represent atomic ratios of Zr, Ni and M, satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Fe; and Fe and at least one selected from the group consisting of V, Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm].
5. An electrode made of a hydrogen-storing alloy produced by utilizing at least a ferrozirconium (Zr-Fe alloy) as a starting material.
6. A method of producing a hydrogen-storing alloy, characterized by using, as a starting material, at least a zircalloy (Zr-Sn alloy).
7. A method of producing a hydrogen-storing alloy, characterized by using, as a starting material, at least a zircalloy (Zr-Sn alloy), wherein said hydrogen-storing alloy is an alloy expressed by a general formula AB_{α} [where, A represents at least one selected from the group consisting of Zr, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Pr, Mn, Nb, Nd, Mo, Al and Si, and B represents one kind selected from the group consisting of: a single substance of Sn; and Sn and at least one selected from the group consisting of Fe, V, Ni, Cr, Mn, Co, Cu, Zn, Al, Si, Nb, Mo, W, Mg, Ca, Y, Ta, Pd, Ag, Au, Cd, In, Bi, La, Ce, Pr, Nd, Th, Sm and Mm (Mm represents a mixture of rare earth elements); α represents a value of from 1.5 to 2.5 , and A and B are different elements], wherein the alloy phase substantially belongs to Laves phase of intermetallic compound with a crystalline structure of hexagon-symmetrical C14 type having crystalline lattice constants of $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type having crystalline lattice constant of $a = 6.92$ to 7.70 .
8. A method of producing a hydrogen-storing alloy according to Claim 7, wherein said alloy or its hydrogenated product contains, as the component A, at least 30 atom % of Zr.
9. A method of producing a hydrogen-storing alloy according to one of Claims 6, 7 and 8, wherein said alloy or its hydrogenated product is expressed by a general formula of $Zr_{\alpha}Ni_{\gamma}M_{\delta}$, [where α , γ and δ represent atomic ratios of Zr, Ni and M satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\gamma + \delta = 1.2$ to 3.7 , while M represents one selected from the group consisting of: a single substance of Sn; and Sn and at least one selected from the group consisting of Fe, V, Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Bi, La, Ce, Mm, Pr, Nd, Th and Sm].
10. An electrode made of a hydrogen-storing alloy produced by utilizing at least a zircalloy (Zr-Sn alloy) as a starting material.
11. A method of producing a hydrogen-storing alloy, characterized by using, as a starting material, at least a ferrovanadium (V-Fe alloy).
12. A method of producing a hydrogen-storing alloy according to claim 11, characterized by using, as a starting material, at least a ferrovanadium (V-Fe alloy), wherein said hydrogen-storing alloy is an alloy expressed by a general formula of AB_{α} or a hydrogenation product thereof [where, A represents at least one selected from the group consisting of Zr, Ti, Hf, Ta, Y, Ca, Mg, La, Ce, Pr, Mn, Nb, Nd, Mo, Al and Si and b represents one selected from the group consisting of: V and Fe; and V, Fe and the balance substantially at least one selected from the group consisting of Ni, Cr, Mn, Co, Cu, Zn, Al, Si, Nb, Mo, W, Mg, Ca, Y, Ta, Pd, Ag, Au, Cd, In, Sn, Bi, La, Ce, Mm, Pr, Nd, Th and Sm (Mm represents a mixture of rare earth elements); α represents a value of from 1.5 to 2.5 ; and A and B are different elements], wherein the alloy phase substantially belongs to Laves phase of intermetallic compound with a crystalline structure of hexagon-symmetrical C14 type having crystalline lattice constants of $a = 4.8$ to 5.2 and $c = 7.9$ to 8.3 and/or cubic-symmetrical C15 type having crystalline lattice constant of $a = 6.92$ to 7.70 .
13. A method of producing a hydrogen-storing alloy according to Claim 12, wherein said ferrovanadium (V-Fe alloy) contains at least 50 atoms % V.
14. A method of producing a hydrogen-storing alloy according to Claim 12, wherein said alloy or its

hydrogenated product contains, as the component A, at least 30 atomic % Zr.

15. A method of producing a hydrogen-storing alloy according to one of Claims 11, 12, 13 and 14, wherein
5 said alloy or its hydrogenated product is expressed by a general formula of $Zr\alpha V\beta Ni\gamma M\delta$, where α , β , γ
and δ represent atomic ratios of Zr, V, Ni and M satisfying the conditions of $\alpha = 0.5$ to 1.5 , $\beta = 0.01$ to
 1.2 , $\gamma = 0.4$ to 2.5 and $\delta = 0.01$ to 1.8 , $\beta + \gamma + \delta = 1.2$ to 3.7 , while M represents one selected from
the group consisting of: a single substance of Fe; and Fe and at least one selected from the group
consisting of Mg, Ca, Y, Hf, Nb, Ta, Cr, Mo, W, Mn, Co, Pd, Cu, Ag, Au, Zn, Cd, Al, Si, In, Sn, Bi, La,
Ce, Mm, Pr, Nd, Th and Sm].
- 10 16. An electrode made of a hydrogen-storing alloy produced by utilizing at least a ferrovanadium (V-Fe
alloy) as a starting material.
- 15
- 20
- 25
- 30
- 35
- 40
- 45
- 50
- 55

FIG. 1

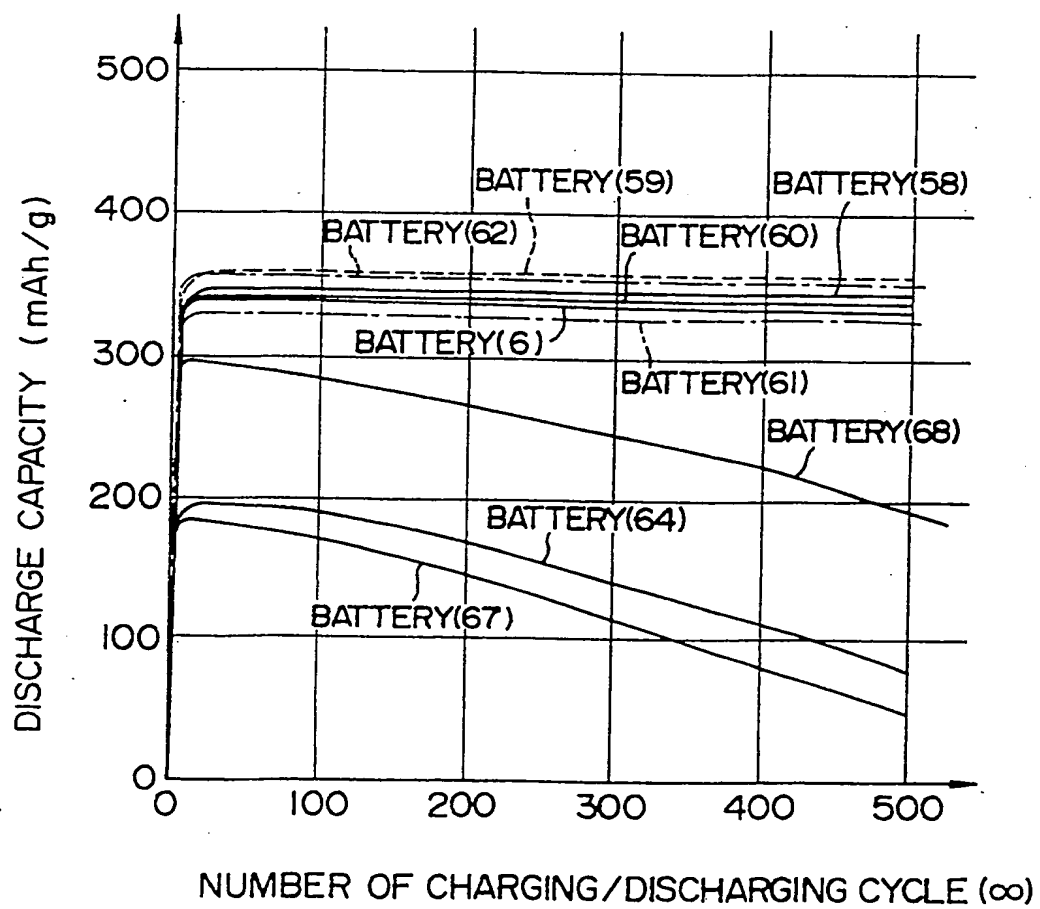
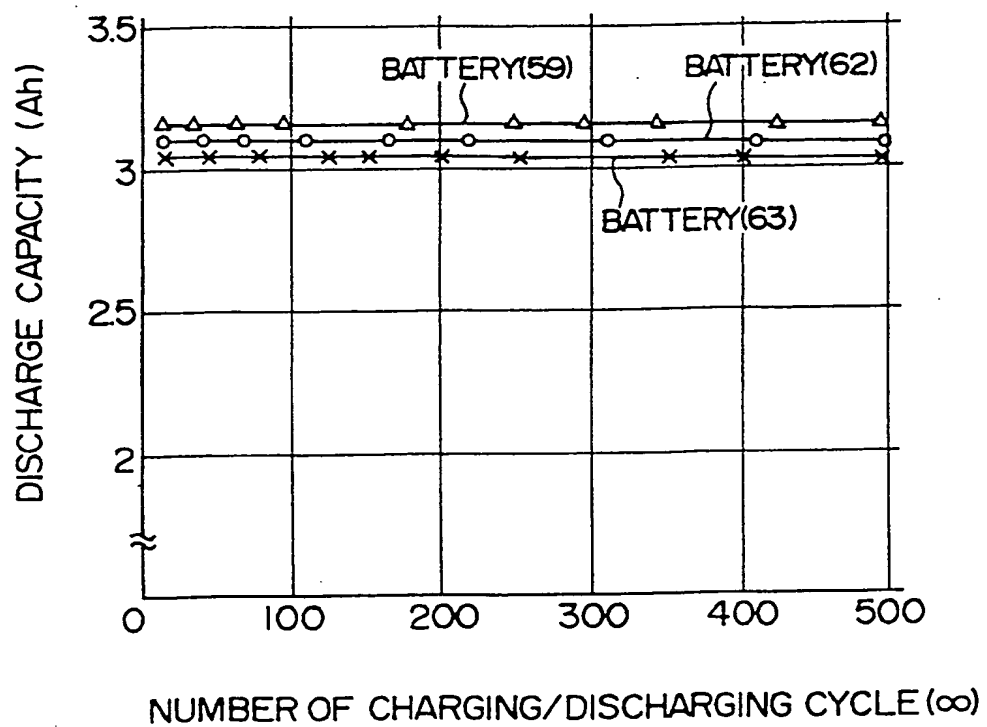


FIG. 2



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/01319

I. CLASSIFICATION F SUBJECT MATTER (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC <div style="display: flex; justify-content: space-between; font-size: 1.2em;"> Int. Cl⁵ C22C1/02, H01M4/38 </div>														
II. FIELDS SEARCHED <div style="text-align: center; font-size: 0.8em;">Minimum Documentation Searched :</div> <div style="display: flex; justify-content: space-between; font-size: 0.8em;"> Classification System : Classification Symbols </div> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> IPC C22C1/02, H01M4/38 </div> <div style="text-align: center; font-size: 0.7em; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *</div>														
III. DOCUMENTS CONSIDERED TO BE RELEVANT * <table border="1" style="width: 100%; border-collapse: collapse; font-size: 0.9em;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>JP, A, 55-122838 (S.A.E.S. Getters S.p.A.), 20 September 1980 (20. 09. 80) & IT, A, 1,110,109 & FR, B1, 2,447,975</td> <td style="text-align: center; vertical-align: top;">1 - 16</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>JP, A, 62-294143 (Mazda Motor Corporation), 21 December 1987 (21. 12. 87), (Family: none)</td> <td style="text-align: center; vertical-align: top;">1 - 16</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>JP, A, 53-85717 (Ugine Aciers), 28 July 1978 (28. 07. 78), (Family: none)</td> <td style="text-align: center; vertical-align: top;">1 - 16</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	JP, A, 55-122838 (S.A.E.S. Getters S.p.A.), 20 September 1980 (20. 09. 80) & IT, A, 1,110,109 & FR, B1, 2,447,975	1 - 16	X	JP, A, 62-294143 (Mazda Motor Corporation), 21 December 1987 (21. 12. 87), (Family: none)	1 - 16	X	JP, A, 53-85717 (Ugine Aciers), 28 July 1978 (28. 07. 78), (Family: none)	1 - 16
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³												
X	JP, A, 55-122838 (S.A.E.S. Getters S.p.A.), 20 September 1980 (20. 09. 80) & IT, A, 1,110,109 & FR, B1, 2,447,975	1 - 16												
X	JP, A, 62-294143 (Mazda Motor Corporation), 21 December 1987 (21. 12. 87), (Family: none)	1 - 16												
X	JP, A, 53-85717 (Ugine Aciers), 28 July 1978 (28. 07. 78), (Family: none)	1 - 16												
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family												
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse; font-size: 0.9em;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">March 19, 1990 (19. 03. 90)</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">April 2, 1990 (02. 04. 90)</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px;"> International Searching Authority <div style="text-align: center;">Japanese Patent Office</div> </td> <td style="width: 50%; padding: 5px;"> Signature of Authorized Officer </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">March 19, 1990 (19. 03. 90)</div>	Date of Mailing of this International Search Report <div style="text-align: center;">April 2, 1990 (02. 04. 90)</div>	International Searching Authority <div style="text-align: center;">Japanese Patent Office</div>	Signature of Authorized Officer								
Date of the Actual Completion of the International Search <div style="text-align: center;">March 19, 1990 (19. 03. 90)</div>	Date of Mailing of this International Search Report <div style="text-align: center;">April 2, 1990 (02. 04. 90)</div>													
International Searching Authority <div style="text-align: center;">Japanese Patent Office</div>	Signature of Authorized Officer													